

PATENT SPECIFICATION

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(54) POLYMER COMBINATIONS USEFUL IN DISTILLATE HYDROCARBON OILS TO IMPROVE COLD FLOW PROPERTIES

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an additive combination of an oil-soluble aliphatic copolymer having the property of a nucleator for wax crystallization e.g., ethylene-vinyl acetate copolymer, with an oil-soluble aromatic copolymer.

Various polymers, useful as middle distillate pour point depressants, prepared from ethylene have been described in the patent literature. These pour depressants include copolymers of ethylene and vinyl esters of lower fatty acids such as vinyl acetate (U.S. Patent 3,048,479); co-polymers of ethylene and alkyl acrylates (Canadian Patent 676,875); terpolymers of ethylene with vinyl esters and alkyl fumarates (U.S. Patents 3,304,261 and 3,341,309); polymers of ethylene (British Patents 848,777 and 993,744); chlorinated polyethylene (Belgian Patent 707,371 and U.S. Patent 3,337,313), etc.

Polymers having alkyl groups in the range of C₄ to C₁₈, such as homopolymers and copolymers of olefins, alkyl esters of unsaturated dicarboxylic acids (e.g., copolymers of dialkyl fumarate with vinyl acetate) and copolymers of olefins and said esters, are known in the art principally as lube oil pour depressants and/or V.I. improvers. For example, U.S. 2,379,728 teaches olefin polymers as lube pour depressants; U.S. 2,460,035 shows polyfumarates; U.S. 2,936,300 shows a copolymer of dialkyl fumarate and vinyl acetate; while U.S. 2,542,542 teaches copolymers of olefins, such as octadecene, with maleic anhydride esterified with alcohol, e.g., lauryl alcohol, in lubes and heating oils.

Synergistic pour point depressing combinations of various members of the above-noted two types of polymers in heavy fuels, e.g., residual and flash distillate fuels, which fuels contain relatively large amounts of waxes having on average 20 or more carbon atoms in the molecules, are taught in U.S. 3,726,653. The cold flow of middle distillate fuels is improved by the additive combination of 1000 to 3000 molecular weight (\bar{M}_n) ethylene copolymer, such as ethylene-vinyl acetate, and the polymer of a lauryl acrylic acid ester according to U.S. 3,275,427.

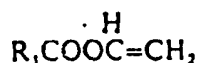
United Kingdom Specification 1,374,051 teaches that the low temperature flow characteristics of hydrocarbon middle distillates can be very satisfactorily controlled by the proper choice of a combination of a nucleating agent or wax growth stimulator and a wax crystal growth arrester.

U.S. 3,449,250 teaches that certain physical as well as some chemical properties of the heavier than gasoline liquid hydrocarbons such as fuel oils and lubricating oils, preferably those that have an initial boiling point of around 260°C., are markedly improved by the addition of a minor amount of a copolymer which imparts stability and detergency to said liquid hydrocarbons. The copolymer has a molecular weight in the range of about 500 to 150,000 and is formed of substantially equimolar portions of maleic anhydride and alpha-olefins such as ethylene, propylene, isobutylene, or styrene. The carboxyl groups of the copolymers are esterified with an aliphatic alcohol to make the copolymer oil

soluble and substantially all of the remainder of the carboxyl groups are imidized.

In accordance with the present invention, a wax containing distillate petroleum fuel oil boiling in the range of 120 to 500°C and having a final boiling point above 370°C which has been improved in its low temperature flow properties containing in the range of 0.001 to 0.5 wt.%, of a synergistic flow and filterability improving combination of:

(a) 1—20 parts by weight of an aliphatic copolymer as a nucleator for wax crystallization in said distillate, wherein said nucleator is a copolymer of ethylene and another monomer selected from a vinyl ester of a monocarboxylic acid having the general formula



wherein R₁ is hydrogen or C₁—C₁₁ alkyl an alpha C₂—C₁₈ monolefin, vinyl chloride, acrylonitrile, and acryamide or a chlorinated polyethylene, said copolymer or polymer having a (Mn) of from 500 to 50,000, said copolymer having 3 to 40 molar portions of ethylene per molar portion of said another monomer and

(b) 1—100 parts by weight of an aromatic oil-soluble copolymer of C₆ to C₂₀ monovinyl aromatic monomer and an ester of an ethylenically unsaturated acid selected from the group consisting of maleic anhydride, maleic acid, fumaric acid acrylic acid and methacrylic acid esterified with a saturated aliphatic alcohol or saturated polyol containing 2 to 10 hydroxy groups the alcohol or polyol having 1 to 60 carbon atoms and/or amide and/or imide of the ethylenically unsaturated acid imidated with an amine containing 1—60 carbon atoms and 1—12 nitrogen atoms, said aromatic copolymer having a number average molecular weight (Mn) of from 500 to 50,000, preferably from 500 to 15,000. It is preferred also that the weight ratio of a/b is in the range of 1/20 to 5/1. For purposes of this disclosure the M is measured by Vapor Phase Osmometry (VPO) from 500 to about 15,000 and by Membrane Osmometry above 15,000.

More specifically, the aromatic copolymer can be characterized as essentially alternating copolymers of styrene and either acrylic acid esters or methacrylic acid esters or derivatized maleic anhydride. In the latter case, the anhydride groups originating from maleic anhydride are derivatized with either aliphatic alcohols and/or amines which will be later described in more detail.

It has been found that said composition prevents oil gelation and effectively controls wax crystal size in distillate hydrocarbon oils having a final boiling point in excess of 370°C.

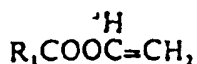
Concentrates of 1 to 60 wt.% of said additive combination in 40 to 99 wt.%, of mineral oil, e.g., kerosene, can be prepared for ease of handling.

The nucleator for wax crystallization is an aliphatic copolymer material which is soluble in the distillate at temperatures above the saturation temperature of the "waxy" components of said distillate but on cooling of the distillate progressively separates out as the temperature of the distillate approaches the saturation point of said "waxy" components, i.e., the distillate is cooled from a point slightly above (e.g., 10°F. above; preferably about 5°F. above) to the temperature below said saturation temperature. The term "saturation temperature" is defined as the lowest temperature at which the crystallization of the solute, i.e. petroleum waxes, cannot be initiated even if crystallization inducement methods are used.

Thus a wax nucleator raises the temperature at which the onset of wax crystallization from said distillate oil (e.g. fuel oil) occurs during cooling and is soluble in said oil at temperatures above the saturation temperature of said wax in said oil, but begins to separate out from said oil as the oil temperature approaches that of said saturation temperature.

Preferred among the polymeric wax nucleators are copolymers with a polymethylene backbone which is divided into segments by hydrocarbon, or oxyhydrocarbon side chains, (usually prepared by free radical polymerization which might result in some branching) and comprises 3 to 40, preferably 4 to 20, molar proportions of ethylene per molar proportion of an ethylenically unsaturated ester monomer (or mixture of unsaturated esters).

The unsaturated ester monomers, copolymerizable with ethylene, are the vinyl esters of C₁ to C₁₈ monocarboxylic acids, preferably C₂ to C₈ monocarboxylic acids, of the general formula:



wherein: R_1 is hydrogen or a C_1 to C_{17} , preferably a C_1 to C_8 , e.g. C_1 to C_4 straight or branched chain alkyl group. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, and vinyl palmitate.

These preferred copolymers are readily produced by conventional polymerization methods using a free radical initiator as in U.S. 3,048,479.

Other monomers that can be copolymerized with ethylene include C_3 to C_{18} alpha monoolefins, which can be either branched or straight chain, such as propylene, isobutene, n-octene-1, isooctene-1, n-decene-1, and dodecene-1. Still other monomers include vinyl chloride (although essentially the same result can be obtained by chlorinating polyethylene, e.g., to a chlorine content of 10 to 35 wt. %), acrylonitrile, and acrylamide. The copolymerization is conventionally obtained using free radical initiators, Ziegler-Natta catalysts, etc.

The preferred copolymers can be formed as follows: solvent, and 5—50 wt. % of the total amount of monomer charge other than ethylene are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to the desired reaction temperature, e.g., 70 to 250°C., and pressured to the desired pressure with ethylene, e.g., 700 to 25,000 psig, usually 900 to 7,000 psig. The initiator, usually dissolved in solvent so that it can be pumped, and additional amounts of the monomers charge other than ethylene, e.g. the vinyl ester, can be added to the vessel continuously, or at least periodically, during the reaction time. Also during this reaction time, as ethylene is consumed in the polymerization reaction, additional ethylene is supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, usually a total reaction time of 1/4 to 10 hours will suffice, the liquid phase is discharged from the reactor and solvent and other volatile constituents of the reaction mixture was stripped off leaving the copolymer as residue. To facilitate handling and later oil blending, the polymer is dissolved in a light mineral oil to form a concentrate usually containing 10 to 60 wt. % of copolymer.

Usually, based upon 100 parts by weight of copolymer to be produced, about 50 to 1200, preferably 100 to 600 parts by weight of solvent, usually a solvent such as benzene, hexane, cyclohexane, and t-butyl alcohol., and about 1 to 20 parts by weight of initiator will be used.

The initiator is chosen from a class of compounds which at elevated temperatures undergo a breakdown yielding radicals, such as peroxide or azo-type initiators, including the acyl peroxides of C_2 to C_{18} branched or unbranched carboxylic acids, as well as other common initiators. Specific examples of such initiators include dibenzoyl peroxide, di-tertiary butyl peroxide, t-butyl perbenzoate, t-butyl peroctoate, t-butyl hydroperoxide, alpha, alpha', azo-diisobutyronitrile, and dilauroyl peroxide. Dilauroyl peroxide is preferred when the polymer is made at a low temperature, e.g., 70 to 135°C., while di-tertiary butyl peroxide is preferred at higher polymerization temperatures.

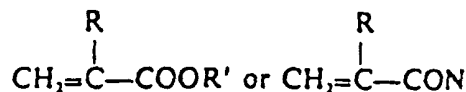
The second component of these flow improvers for distillate oils are oil-soluble copolymers of a monovinyl aromatic monomer, e.g. styrene, and at least one ethylenically unsaturated polar monomer usually containing from 8 to 52 carbons, preferably 10 to 32 carbons and consisting of carbon, hydrogen and/or oxygen, and/or nitrogen, and optionally halogen and/or sulfur.

The monovinyl aromatic monomer useful herein is preferably a C_8 to C_{20} monovinyl aromatic compound including alpha-methylstyrene and the preferred species styrene.

The oil-soluble derivatives of said copolymers of a monovinyl aromatic monomer and a polar monomer can be obtained either by derivatizing said polar monomer and thereafter copolymerizing or by derivatising said copolymers. In the case of acidic polar monomers such as acrylic or methacrylic acids it is customary to first derivatize them, e.g. to esters, amides or ester-amides, and then copolymerize with a vinyl aromatic monomer. On the other hand, when maleic anhydride is used as a comonomer it is preferred to copolymerize it with the monovinyl aromatic monomer and then to derivatize the already so formed copolymer on its anhydride sites. The derivatization can be accomplished using alcohols containing from 1 to 60 carbons thus forming esters, amines containing from 1 to 60 carbons and 1 to 12 nitrogen atoms thus forming amides or any ratio of said alcohols and said amines thus forming ester-amide derivatives.

A particularly useful class are oil-soluble derivatives of copolymers of a monovinyl aromatic monomer having from 8 to 20 carbons in the molecule, e.g. styrene and a dicarboxylic acid material (either as an anhydride such as maleic anhydride or a dicarboxylic acid such as fumaric acid or maleic acid). More usually the styrene-maleic anhydride copolymers are formed by copolymerization of substantially equimolar amounts of the monomers. The resulting copolymers after derivatization have a \bar{M}_n in the range of 500 to 150,000 as have the acrylate copolymers.

Another particularly useful class of the oil-soluble derivatives are the acrylate copolymers of a C_8 to C_{20} monovinyl aromatic monomer, e.g. styrene and acrylic or methacrylic derivatives represented by the formulae:

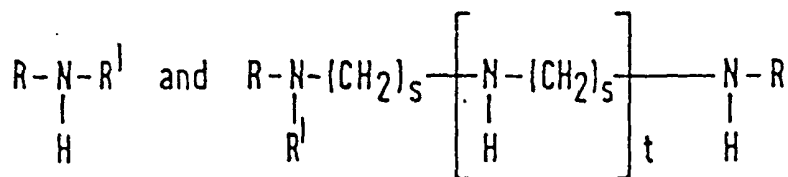


wherein R represents hydrogen or methyl, R' represents alkyl group of 8 to 24 carbon atoms and N represents an amine containing 1 to 60 carbon atoms and 1 to 12 nitrogen atoms. The alkyl group of R' is preferably essentially straight chain and contains 12 to 18 carbon atoms although methyl and ethyl branching can be tolerated. The acrylic or methacrylic monomers from which the copolymer is derived includes alkyl acrylate, alkyl methacrylate, alkyl amino-acrylates and alkyl aminomethacrylates such as lauryl acrylate, lauryl methacrylate and N,N-dimethylaminoethyl methacrylate.

The alcohols suitable for use in producing the esters of the copolymer of a monovinyl aromatic monomer, e.g., styrene and a dicarboxylic acid material, e.g. maleic anhydride are generally aliphatic alcohols having from 1 to 60 carbons per molecule. Saturated aliphatic alcohols containing 6 to 22 carbon atoms per molecule are preferred. Examples of alcohols suitable for use in producing the esters include straight chain normal primary alcohols such as ethyl, propyl, butyl, hexyl, octyl, lauryl, octadecyl, eicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, and hexacosyl. Polyols containing from 2 to 10 hydroxy groups can be utilized as well, e.g. glycerol, alkylene glycols such as dipropylene glycol, trimethylol methane and pentaerythritol.

Commercially available mixtures of alcohols consisting essentially of saturated alcohols of the requisite chain length may be employed in preparing the long chain esters. One such mixture is marketed under the trade name Behenyl alcohol and is a mixture of C_{16} — C_{22} alcohols derived from natural sources.

Useful amine compounds for amination/imidation of the copolymers according to this invention include mono- and polyamines of 1 to 60, e.g., 3 to 20, total carbon atoms and 1 to 12, e.g. 2 to 6 nitrogen atoms in the molecule, which amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g., hydroxy groups, alkoxy groups, amide groups, and imidazoline groups. Preferred amines are aliphatic, primary and secondary amines including polyamines. It is possible to substitute up to 25 mole percent of said amines with primary or secondary aromatic amines. The preferred amines include those of the general formulae:

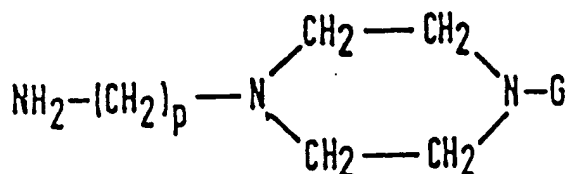


wherein R and R' are independently selected from the group consisting of C_1 to C_{12} straight or branched chain alkyl radicals, C_1 to C_{12} alkoxy C_1 to C_6 alkylene radicals, C_2 to C_{12} hydroxy or amino alkylene radicals, and C_1 to C_{12} alkylamino C_2 to C_6 alkylene radicals, and R' can also be hydrogen, s is a number of from 2 to 6, preferably 2 to 4; and t is a number of from 0 to 10, preferably 2 to 6.

Non-limiting examples of suitable amine compounds include: mono- and di-tallow amines; 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; diethylene triamine; triethylene tetraamine; tetraethylene pentamine; 1,2-propylene diamine; di-(1,2-propylene) triamine; di-(1,3-propylene)

triamine; N,N-dimethyl-1,3-di-aminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N - di - (2 - hydroxyethyl) - 1,3 - propylene diamine; 3-dodecyloxy-propylamine; N-dodecyl-1,3-propane diamine, tris-hydroxy-methyl methylamine, diisopropanol amine, and diethanol amine.

Other useful amine compounds include: alicyclic diamines such as 1,4-di-(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines and N-aminoalkyl piperazines of the general formula:



wherein G is independently selected from the group consisting of hydrogen and omega-aminoalkylene radicals of from 1 to 3 carbon atoms; and p is an integer of from 1 to 4. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine; N-(3-aminopropyl) piperazine; and N,N'-di-(2-aminoethyl) piperazine.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and isomeric piperazines. Low cost poly(ethylene amines) compounds having a composition approximately tetraethylene pentamine are available commercially under the trade name Polyamine 400 (PA-400), marketed by Jefferson Chemical Co., New York, New York. Similar materials may be made by the polymerization of aziridine, 2-methyl aziridine and azetidene.

Still other amines separated by hetero atom chains such as polyethers or sulfides can be used.

Also included are primary and secondary amines having 2 to 3 hydroxy groups such as tris-hydroxymethyl amino-methane, diisopropanolamine, 2-amino - 2 - methyl - 1,3 - propane diol and 2 - amino - 2 - ethyl - 1,3 - propane diol.

The method of making monovinyl aromatic copolymers and the esterification and/or amidation and/or imidation thereof using alcohol and amines is quite adequately broadly described in the prior art in U.S. 2,615,845. The polymerization of the monovinyl aromatic monomer and ethylenically unsaturated esterified (including the partially esterified) monomer can be conducted by free radical initiated polymerization techniques as those earlier set forth in this specification with regard to preparation of the nucleator for wax crystallization.

The distillate hydrocarbon oils which are treated with the additive package of this invention are wax-containing distillate petroleum oils boiling in the range of 120 to 500°C.

The invention is particularly effective for the cold flow treatment of high end point fuels which are non-responsive to conventional flow improvers, i.e., those fuels having a final boiling point above 370°C. (ASTM-1160).

EXAMPLES

The following materials were used:

Polymer 1

Polymer 1 is a copolymer of ethylene and vinyl acetate produced as outlined in U.K. Specification 1,374,051 and having Mn of about 4100, a vinyl acetate content of 9 wt.% and a specific viscosity of 0.37. This copolymer is also described in U.S. Patent 3,961,916 (corresponding to said U.K. Specification) as copolymer K.

Polymer A

Polymer A was a styrene-maleic anhydride copolymer which has been esterified with aliphatic alcohols and amidized with an alkylamine dissolved in

mineral oil and purchased as HiTec (Registered Trade Mark) 672 from Monsanto Chemical Co. of St. Louis, Missouri. The solution is believed to contain 33% by weight of said copolymer having a Mn of about 14,800 and composed of 78.37 wt.% carbon, 10.93 wt.% hydrogen and 0.38 wt.% nitrogen. The linear primary alcohols of said copolymer are believed to have from 10 to 18 carbons.

Polymer B

Polymer B was a copolymer of styrene and lauryl methacrylate dissolved in mineral oil and purchased as Santopour (Registered Trade Mark) C from Monsanto Chemical Co. of St. Louis, Missouri.

The Fuel

The properties of the distillate fuel oils tested are summarized in Table I which follows:

		Distillate Fuels	
		A	B
Cloud Point, °C.		-2	+5
n Paraffin Range, C#		18—34	16—38
Distillation, °C. (per ASTM-D-1160)			
IBP		161.1	178.9
FBP		416	453

Various blends of Polymer I with Polymers A and B in the fuel were made by simply dissolving polymer in the fuel oil. This was done while warming, e.g., heating the oil and polymer to about 90°C. if the polymer per se was added, and stirring. In other cases, the polymer was simply added with stirring to the fuel in the form of an oil concentrate which was usually about 50 wt.% polymer dissolved in a light mineral oil.

The blends were then tested for their cold flow properties in the tests described below.

The Cold Filter Plugging Point Test (CFPPT)

The cold flow properties of the blend were determined by the Cold Filter Plugging Point Test (CFPPT). This test is carried out by the procedure described in detail in "Journal of the Institute of Petroleum," Volume 52, Number 510, June 1966 pp. 173—185. In brief, a 40 ml. sample of the oil to be tested is cooled by a bath maintained at about -34°C. Periodically (at each one degree Centigrade drop in temperature starting from 2°C. above the cloud point) the cooled oil is tested for its ability to flow through a fine screen in a time period. This cold property is tested with a device consisting of a pipette to whose lower end is attached an inverted funnel positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area of about 0.45 square inch. The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml. of oil. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds. The results of the test are reported as the temperature in °C. at which the oils fail to fill the pipette in the prescribed time.

Imperial Filterability Test (IFT)

In this test a 200 ml sample of oil is cooled at a rate of 1°F./hr. from 5.6°C above to 2.8°C. below its true cloud point at which temperature the oil is passed under 12 inches of water vacuum through a filter element provided with a screen. The Imperial Filterability is reported in terms of the finest screen through which at least 90% of sample will pass under a suction of 12 inches of water in time not exceeding 25 seconds. The true cloud point employed in IFT as the reference point is the temperature at which the formation of wax crystals is first observed when a sample of oil is cooled under stirring at a rate of 20°F./hr.

The blends prepared and the test results are summarized in Table II which follows:

TABLE II
Effectiveness of Polymers in the Fuel

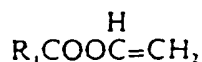
	Example	Polymer	Oil A		Oil B		
			CFPPT°C.	IFT Mesh passed	CFPPT°C.	IFT Mesh passed	
5	1	None	20	20	1.1	80	5
	2	0.02% Polymer I	-12	100	—	—	
	3	0.02% Polymer A	0	100	—	—	
	4	0.02% Polymer B	-10	270	—	—	
10	5	0.01% Polymer I	-13	270	—	—	10
	6	0.01% Polymer A	-16	270	—	—	
	7	0.01% Polymer B					
	8	0.05% Polymer I	—	—	-3	100	
15	9	0.05% Polymer A	—	—	-2	60	15
	10	0.05% Polymer B	—	—	-9	60	
	11	0.025% Polymer I	—	—	-10	270	
20		0.025% Polymer A	—	—	-16	270	20
		0.025% Polymer B					

The synergistic results obtained by the teachings of this invention are apparent from the foregoing Table II, e.g., in Oil A the blend of Example 2 gives a CFPPT of -12°C., the blend of Example 4 gives a CFPPT of -10°C., whereas 50/50 mixtures of the blends of Examples 2 and 4 (Example 6) give a markedly lower CFPPT of -16°C. (similarly synergism is apparent in the results of Examples 2, 3 and 5 whereby the CFPPT is lowered to -13°C); and in Oil B the blend of Example 7 gives a CFPPT of -3°C., the blend of Example 9 gives a CFPPT of -9°C., whereas 50/50 mixtures of the blends of Examples 7 and 9 give a CFPPT of -16°C.; (see Example 11).

WHAT WE CLAIM IS:—

1. A wax-containing distillate petroleum fuel oil boiling in the range of 120 to 500°C. and having a final boiling point above 370°C., which has been improved in its low temperature flow properties, containing in the range of .001 to 0.5 wt.%, based on the weight of the total composition, of a synergistic flow and filterability improving combination of:

(a) 1—20 parts by weight of an aliphatic copolymer functioning as a nucleator for wax crystallization in said distillate, wherein said nucleator is a copolymer of ethylene and another monomer selected from a vinyl ester of a monocarboxylic acid having the general formula



wherein R_1 is hydrogen or C_1 — C_{17} alkyl, an alpha C_3 — C_{16} monoolefin, vinylchloride, acrylonitrile, and acrylamide or a chlorinated polyethylene said copolymer or polymer having a (\overline{M}_n) of from 500 to 50,000, said copolymer having 3 to 40 molar proportions of ethylene per molar proportion of said another monomer, and

(b) 1—100 parts by weight of an aromatic oil soluble copolymer of C_8 to C_{30} monovinyl aromatic monomer and an ester of an ethylenically unsaturated acid selected from the group consisting of maleic anhydride, maleic acid, fumaric acid acrylic acid and methacrylic acid, esterified with a saturated aliphatic alcohol or saturated polyol containing 2 to 10 hydroxy groups, the alcohol or polyol having 1 to 60 carbon atoms and/or amide and/or imide of the ethylenically unsaturated acid amidated and/or imidated with an amine containing 1—60 carbon atoms and 1—12 nitrogen atoms said aromatic copolymer having a number average molecular weight (\overline{M}_n) in the range of 500 to 50,000.

2. A fuel oil according to claim 1 wherein said vinyl ester is vinyl acetate.

3. A fuel oil according to claims 1 or 2 wherein said aromatic monomer is styrene and said ester is maleic anhydride ester.

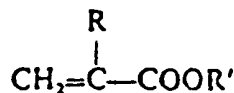
4. A fuel oil according to claims 1 or 2 wherein said aromatic monomer is styrene and said ester is a methacrylate.

5. A fuel oil according to claim 4 wherein said methacrylate is lauryl methacrylate.

6. A wax-containing distillate petroleum fuel oil boiling in the range of 120 to 500°C. and having a final boiling point above 370°C., which has been improved in its low temperature flow properties, containing in the range of .001 to 0.5 wt.%, based on the weight of the total composition, of a synergistic flow improving combination of:

(a) copolymer consisting essentially of ethylene with 0.3 to 12 mole percent of vinyl acetate, said copolymer having a number average molecular weight within the range of 1500—30,000, and

(b) oil-soluble copolymer having a number average molecular weight in the range of 500 to 50,000 of styrene and ester of the formula:



wherein R represents hydrogen or methyl; and R' represents a straight chain alkyl group of 12 to 18 carbon atoms, and wherein the weight ratio of (a)/(b) is in the range of 1/20 to 5/1.

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